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(54) Title: A CLEANING COMPOSITION COMPRISING BLEACH, SULPHAMIC ACID, AND A POLYCARBOXYLATE POLYMER

(57) Abstract

There is provided a cleaning composition comprising a halogen bleach and an organic or inorganic $-NH_2$ compound and a polycarboxylate polymeric compound, whereby reduced skin irritation as well as effective bleach malodour reduction are obtained.

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A CLEANING COMPOSITION COMPRISING BLEACH, SULPHAMIC ACID, AND A POLYCARBOXYLATE POLYMER

Field of the invention

The present invention relates to a cleaning composition, and more particularly to cleaning compositions with reduced skin irritation and effective bleach malodour reduction.

Background of the invention

Halogen bleaches, in particular hypochlorite, are known to be some of the most effective hygiene agents, especially at low concentrations, and are available in commercial quantities at acceptable cost. Halogen bleaches provide a hygiene benefit against a wide range of microbes including bacteria, moulds, yeast and fungi. Thus, it is highly desirable to incorporate halogen bleaches in detergent compositions for bleaching and/or disinfection purposes. However, halogen bleaches and in particular hypochlorite are irritant and many consumers suffer from skin irritation when using such compositions.

Particularly, the hands of the user are prone to such irritation. As a result of coming into contact with such compositions the hands suffer from dryness and from a feeling of tightness. This occurs when the compositions are used neat and also when used in diluted form.

Without being limited by theory, it is believed that halogen bleaches like hypochlorite attack the uppermost layer of the epidermal of the skin. This results in the decrease of the elasticity of the skin. The skin also becomes more sensitive, resulting in dryness and coarseness of the skin. In addition, the skin may become inflamed and become red, sore and itchy. These effects are magnified in alkaline conditions, because alkali is also an irritant. Alkalinity is required for example for optimum hypochlorite stability, thus alkaline pH is the preferred condition for hypochlorite-comprising compositions. However, alkaline conditions

contribute to skin tightening because they alter the natural pH of the skin.

Accordingly, it is an object of the present invention to reduce skin irritation of halogen bleach-comprising compositions.

Still another problem encountered with the use of halogen bleach is the resulting bleach malodour.

Accordingly, it is another object of the present invention to reduce bleach malodour of halogen bleach-comprising compositions.

To overcome such a problem of bleach malodour, organic or inorganic -NH_2 compounds have been used in halogen bleach compositions. A typical disclosure can be found in the pending application PCT/US96/01908 filed March 3, 1995.

The Applicant has now surprisingly found that the provision of a polycarboxylate polymer in a cleaning composition comprising a halogen bleach and an organic or inorganic -NH_2 compound provides reduced skin irritation while still providing said halogen bleach compositions with effective bleach malodour reduction. Indeed, it has been found that a reduction in the skin irritation as well as an effective bleach malodour reduction was obtained with the compositions of the invention compared to halogen bleach compositions containing an organic or inorganic -NH_2 compound but no polycarboxylate polymer.

Polycarboxylate polymeric compounds are known in the art as thickening components., A typical disclosure can be found in WO 94/10272.

Accordingly, an advantage of the compositions according to the invention is their reduced skin irritation as well as their effective bleach malodour reduction compared to halogen bleach compositions containing an organic or inorganic -NH_2 compound but no polycarboxylate polymer.

Still a further advantage of the compositions of the invention is their effective cleaning performance.

By "effective", it is meant that compositions of the invention provide at least equal performance compared to halogen bleach compositions containing an organic or inorganic $-NH_2$ compound but no polycarboxylate polymer.

Summary of the invention

The present invention is a cleaning composition comprising a halogen bleach and an organic or inorganic $-NH_2$ compound, characterised in that said composition further comprises a polycarboxylate polymer.

In another aspect of the invention, the present invention encompasses the use of said polycarboxylate polymeric compound in a cleaning composition comprising a halogen bleach and an organic or inorganic $-NH_2$ compound for providing reduced skin irritation.

Detailed description of the invention

Halogen bleach

A halogen bleach is an essential ingredient of the present invention. Common among these types of bleaches are the alkali metal and alkali earth metal hypochlorites, hypobromites and hypoiodites although other bleaches that are organic based sources of halide, such as chloroisocyanurate, are also applicable. A preferred bleach has the formula $M(OX)_y$ where : M is a member selected from the group consisting of sodium, lithium, potassium, magnesium, calcium, and mixtures thereof; O is an oxygen atom; X is a member selected from the group consisting of chlorine, bromine, iodine, and mixtures thereof; and y is 1 or 2 depending on the charge of M.

Preferred halogen bleaches for use herein are sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, sodium hypobromite, potassium hypobromite, calcium hypobromite, magnesium hypobromite, sodium hypoiodite and potassium hypoiodite, more preferably sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, most preferably sodium hypochlorite.

The compositions of the present invention typically comprise from 0.01% to 10% by weight of the total composition of said halogen bleach or mixtures thereof, preferably from 0.01% to 5%, more preferably from 0.1% to 2.5%, and most preferably from 0.5% to 2.5% by weight.

Organic or inorganic $-NH_2$ compound

Another essential ingredient of the present invention is an organic or inorganic derived $-NH_2$ compound, or mixtures thereof. Said organic and inorganic derived $-NH_2$ compounds are effective in reducing or eliminating the irritation of the skin of the user, when a halogen bleach-containing composition comprising it comes into contact with the skin. Still another advantage to the use of said organic or inorganic derived $-NH_2$ compound is their property in reducing the bleach malodour on skin, so called "bleach hand smell". Examples of such compounds are sulphamic acid, sulphamide, p-toluenesulphonamide, imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamides, and mixtures thereof. At pH levels greater than 11, the above mentioned compounds may be de-protonated, that is, they may be in the form of a salt and therefore due to expediency, ease of synthesis or preparation, or due to formulation practices the salt form of any or all of the above mentioned compounds will suffice. Although any suitable cation will suffice for the purposes of the present invention, sodium, potassium, lithium, magnesium, calcium, and mixtures thereof are preferred. Accordingly, the organic or inorganic derived $-NH_2$ compound is preferably a member selected from the group consisting of sulphamic acid, sodium sulphamate, potassium sulphamate, sulfamide, p-toluenesuphonamide, imidodisulphonamide, benzenesulphonamide,

melamine, cyanamide, alkyl sulfonamide, and mixtures thereof and more preferably is sulphamic acid.

The present invention comprises said -NH_2 compound in an amount such that the molar ratio of said halogen bleach to said -NH2 compound is preferably from 10:1 to 1:10, more preferably from 5:1 to 1:2, most preferably from 3:1 to 1:2.

Polycarboxylate polymer

Another essential component of the present invention is a polycarboxylate polymer. The polycarboxylate polymers, contrary to cellulosic polymers such as guar gum or xanthum gum, are more stable in presence of halogen bleaches and provide a higher yield value. Not to be bound by theory, it is believed that the polycarboxylate polymer forms a hydrophobic film on the hands surface. As a result, the contact with the water phase containing the halogen bleach is reduced; which thus, slows the kinetics of reaction between the halogen bleach and the skin amino acid.

Suitable polymers for use herein are polymers comprising monomeric units selected from the group consisting of unsaturated carboxylic acids such as acrylic acid, polycarboxylic acids, sulphonic acids, phosphonic acids and mixtures thereof. Copolymerisation of the above monomeric units among them or with other co-monomers such as maleic anhydride, ethylene or propylene are also suitable. When used, maleic anhydride will acts as a source of additional carboxylic groups, whilst ethylene and propylene will act as diluents.

The molecular weight per carboxylate group of monomers containing a carboxylate group typically varies from 25 to 200, preferably from 50 to 150, more preferably from 75 to 125. Preferred polymers for use herein have a total molecular weight of from 500,000 to 4,500,000, preferably from 1,000,000 to 4,000,000. Most preferred polymers for use herein contain from 0.5% to 4% by weight of a cross-linking agent, wherein the cross-linking agent tends to interconnect linear strands of the polymers to form the resulting cross-linked products. Suitable cross-linking agents include the polyalkenyl polyethers.

Preferred polycarboxylate polymers for use herein are the polyacrylate polymers. Commercially available polymers of the polyacrylate type include those sold under the trade names Carbopol®, Acrysol® ICS-1, Polygel®, and Sokalan®. Most preferred polyacrylate polymers are the copolymer of acrylic acid and alkyl (C_5-C_{10}) acrylate, commercially available under the tradename Carbopol® 1623, Carbopol® 695 from BF Goodrich, and copolymer of acrylic acid and maleic anhydride, commercially available under the tradename Polygel® DB from 3V Chemical company.

Mixtures of any of the polycarboxylate polymers, herein before described, may also be used.

The polycarboxylate polymer is preferably present in an amount of from 0.01% to 5% by weight, more preferably 0.4% to 1.5% by weight, most preferably 0.5% to 1% by weight of the composition.

Optional

The compositions according to the present invention may comprise a number of optional ingredients such as surfactants, buffers, perfumes, bleach boosters, fatty acids, radical scavengers, chelants, antimicrobial compounds, builders, bactericides, solvents, enzymes, hydrotropes, colorants, bleach activators, soil suspenders, dye transfer agents, brighteners, anti dusting agents, dispersants, dye transfer inhibitors, pigments and dyes. Naturally, for the purpose of the invention, the optional ingredients have to be stable to halogen bleaches.

Surfactants

Suitable surfactants for use herein are selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic surfactants. When used, the surfactants will be present in an amount of from 0.1% to 95% by weight of a surfactant, preferably from 0.1% to 20% by weight.

Suitable anionic surfactants include anionic surfactants that can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfonation reaction products having in their molecular structure an alkyl radical containing from about 6 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the anionic synthetic detergents which can form the surfactant component of the compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_{6-18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid ester of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut alcohols) and about 1 to about 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids are derived from coconut oil sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Additionally, secondary alkyl sulfates may be used by the formulator exclusively or in conjunction with other surfactant materials and the following identifies and illustrates the differences between sulfated surfactants and otherwise conventional alkyl sulfate surfactants. Non-limiting examples of such ingredients are as follows.

Conventional primary alkyl sulfates, such as those illustrated above, have the general formula ROSO3-M+ wherein R is typically a linear C_6-C_{22} hydrocarbon group and M is a water solubilizing cation. Branched

chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 8-20 carbon atoms are also known; see, for example, EP 439 316.

Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbon "backbone" of the molecule. Such materials may be depicted by the structure

$$CH_3(CH_2)_n(CHOSO_3^-M^+)(CH_2)_mCH_3$$

wherein m and n are integers of 2 of greater and the sum of m+n is typically about 9 to 17, and M is a water-solubilizing cation.

In addition, the selected secondary (2,3) alkyl sulfate surfactants used herein may comprise structures of formulas I and II

$$CH_3(CH_2)_x(CHOSO_3^-M^+)CH_3$$

I

$$CH_3(CH_2)_y(CHOSO_3^-M^+)CH_2CH_3$$

II

for the 2-sulfate and 3-sulfate, respectively. Mixtures of the 2- and 3-sulfate can be used herein. In formulas I and II, x and (y+1) are, respectively, integers of at least about 6, and can range from about 7 to about 20, preferably from about 10 to about 16. M is a cation, such as an alkali metal, ammonium, alkanolammonium, triethanol-ammonium, and the like, can also be used.

The aforementioned secondary alkyl sulfates are those prepared by the addition of H2SO4 to olefins. A typical synthesis using alpha olefins and sulfuric acid is disclosed in U.S. Pat. No. 3,234,258, Morris, issued February 8, 1966 or in U.S. Pat. No. 5,075,041, Lutz, issued December 24, 1991. The synthesis conducted in solvents which afford the secondary (2,3) alkyl sulfates on cooling, yields products which, when purified to remove the unreacted materials, randomly sulfated materials, unsulfated by-products such as C10 and higher alcohols, secondary

olefin sulfonates, and the like, are typically 90+% pure mixtures of 2- and 3-sulfated materials (some sodium sulfate may be present) and are white, non tacky, apparently crystalline, solids. Some 2,3-disulfates may also be present, but generally comprise no more than 5% of the mixture of secondary (2,3) alkyl mono-sulfates. Such materials are available under the name "DAN", e.g. "DAN 200" from Shell Oil Company.

Other suitable surfactants to be used herein include amine oxides according to the formula $R_1R_2R_3NO$ where R_1 is primarily a C_6-C_{22} alkyl group and R_2 and R_3 are C_1 to C_3 alkyl groups or mixtures thereof. Indeed, such amine oxides for use herein can be Genaminox^R LA, Gemaminox^R MY-X (available from Hoechst), C_{12}-C_{14} Aromox^R DMMCO-W, (AKZO), Aromox DM14D-W, (AKZO) and Aromox DM14D-W (AKZO). Suitable amine oxides for use herein are preferably halogen bleach compatible.

Buffers

Buffers can be included in the formulations herein for a variety of purposes. One such purpose is to adjust the cleaning solution pH to optimize the hard surface cleaner composition's effectiveness relative to a particular type of soil or stain. Buffers may be included to stabilize the adjunct ingredients with respect to extended shelf life or for the purpose of maintaining compatibility between various aesthetic ingredients. The hard surface cleaner of the present invention optionally contains buffers to adjust the pH in a preferred range above 11. Non-limiting examples of such suitable buffers are potassium carbonate, sodium carbonate, and trisodium phosphate, however, the formulator is not restricted to these examples or combinations thereof.

Perfumes

Perfumes are an optional but highly preferred ingredient especially for the liquid composition embodiment. Perfume is usually used at levels of from 0% to 5%. In U.S 4,246,129, certain perfume materials are

disclosed which perform the added function reducing the solubility of anionic sulfonate and sulfate surfactants.

Bleach boosters

As a further optional, but preferred ingredient, the present compositions comprise bleach boosters. Bleach boosters are those compounds that in an alkaline pH environment are capable of releasing a halide ion, undergoing an oxidation, a reduction or other disproportionation that otherwise yields an activated halide ion. Typically boosters containing bromine atoms and iodine atoms are used in the presence of chlorine atom based bleaches and iodine is used when bromine based bleaches are employed as the primary bleaching agent. Preferred bleach booster has the formula $M(X)_y$ where : a) M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, zinc, and mixtures thereof; and b) X is the radical bromide, hypobromite, bromate, iodide, hypoiodite, iodate, and mixtures thereof; wherein y is 1 or 2.

While not wishing to be limited by theory, it is believed that the boosters have the effect, as in the case of hypochlorite based bleach, of converting the hypochlorite bleach into a more reactive and/or a more stable species, for example, hypobromite, thus providing for the full utility of the bleach formulated. Bleach boosters of the present invention may be added as a precursor which itself can be a bleach booster, for example, iodide ion is a suitable bleach booster according to the present invention. The boosters thus formed by oxidation/reduction or other disproportionations, for example, iodate, may be instead added directly.

The bleach boosters of the present invention are of the formula MX where M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, and zinc while the X is halogen. The preferred bleach boosters are the sodium and potassium salts of bromine and iodine, more preferably sodium and potassium bromide and iodide.

Fatty acids

Another optional component of the present invention is an alkali metal salt of a C_8-C_{18} fatty acid. Said fatty acids are used as suds suppressors. Suitable fatty acids for use herein can be any C_8-C_{18} fatty acid, preferably fully saturated, preferably a sodium, potassium or lithium salt, more preferably the sodium salt. Suitable fatty acids may be selected from caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid and mixtures of fatty acids suitably hardened, derived from natural sources such as tallow, coconut oil, ground oil and babassu oil. Compositions according to the present invention comprise from 0.1% to 2%, preferably less than 0.6% by weight of the composition of fatty acids.

Radical scavenger

A further optional component of the present invention is a radical scavenger. Said radical scavengers are used as stabilisers. A suitable radical scavenger for use herein is the aromatic molecule containing a carboxylic group ring substitution. Suitable examples of radical scavengers for use herein include the meta and para-chlorobenzoic acid, benzoic acid, meta- ortho- and para-methoxybenzoic acid, meta nitrobenzoic acid, para bromobenzoic acid, salicylic acid, 5-sulphosalicylic acid, 3,5-dimethyl salicylic acid and paratoluic acid. Of the above materials, ortho-methoxybenzoic acid is preferred. Compositions according to the present invention comprise from 0.01% to 1.5% by weight, preferably from 0.1% to 0.8% by weight and more preferably from 0.2% to 0.5% by weight of the composition of radical scavengers.

The compositions according to the present invention may be in liquid form. Said liquid compositions are preferably but not necessarily formulated as aqueous compositions, which preferably comprise from 80% to 95%, more preferably from 85% to 90% of water.

Still another optional requirement of the liquid compositions according to the present invention is that the pH is greater than 10, preferably greater than 11, more preferably greater than 12. This is achieved by

the addition of from 0.4% to 3% of a caustic alkali. Suitable caustic alkalis for use herein include sodium and potassium hydroxide. Compositions according to the present invention comprising hypochlorite preferably have a pH greater than 12 for hypochlorite stability.

Packaging form of the compositions

The compositions herein may be packaged in a variety of suitable detergent packaging known to those skilled in the art. The liquid compositions herein may desirably be packaged in manually operated spray dispensing containers, which are usually made of synthetic organic polymeric plastic materials. Accordingly, the present invention also encompasses liquid cleaning compositions of the invention packaged in a spray dispenser, preferably in a trigger spray dispenser. Indeed, said spray-type dispensers allow to uniformly apply to a relatively large area of a surface to be cleaned the liquid cleaning compositions suitable for use according to the present invention; thereby contributing to the cleaning properties of said compositions. Such spray-type dispensers are particularly suitable to clean vertical surfaces.

Suitable spray-type dispensers to be used according to the present invention include manually operated foam trigger-type dispensers sold for example by Specialty Packaging Products, Inc. or Continental Sprayers, Inc. These types of dispensers are disclosed, for instance, in US-4,701,311 to Dunnining et al. and US-4,646,973 and US-4,538,745 both to Focarracci. Particularly preferred to be used herein are spray-type dispensers such as T 8500® commercially available from Continental Spray International or T 8100® commercially available from Canyon, Northern Ireland. In such a dispenser the liquid composition is divided in fine liquid droplets resulting in a spray that is directed onto the surface to be treated. Indeed, in such a spray-type dispenser the composition contained in the body of said dispenser is directed through the spray-type dispenser head via energy communicated to a pumping mechanism by the user as said user activates said pumping mechanism. More particularly, in said spray-type dispenser head the composition is

forced against an obstacle, e.g. a grid or a cone or the like, thereby providing shocks to help atomise the liquid composition, i.e. to help the formation of liquid droplets.

The present invention also encompasses the use of said polycarboxylate polymeric compound in a cleaning composition comprising a halogen bleach and an organic or inorganic $-NH_2$ compound for providing reduced skin irritation. As described hereinbefore, by "reduced skin irritation", it is meant that compositions according to the invention provide a further reduction in the skin irritation compared to halogen bleach compositions containing an organic or inorganic $-NH_2$ compound but no polycarboxylate polymer.

The present invention further encompasses a method for cleaning a hard surface by applying on said surface an effective amount of a composition of the invention. The said composition may be applied in its neat form or after having been diluted with water. Preferably said composition is diluted up to 200 times its weight of water, preferably into 50 to 150 times its weight of water and more preferably 75 to 95, before it is applied to said surface. When the composition is diluted prior to use (to reach a total active level in the order of 1.2%), the composition will still advantageously provide effective cleaning performance. In the preferred embodiment of the method of the present invention wherein said composition is applied to a hard-surface to be cleaned in its diluted form, it may not be necessary to rinse the surface after the composition has been applied.

In the compositions of the invention, the abbreviated component identifications have the following meanings:

C8 AS : Octyl sulphate, available from Albright and Wilson, under the tradename Empimin® LV33

24 AS : Sodium C_{12} - C_{14} alkyl sulphate, available from Albright and Wilson, under the tradename Empicol® 0298/F

Amine oxide : C_{12} - C_{14} amine oxide, commercially available under the tradename Genaminox® LA from Hoechst

Polymer * : Copolymer of acrylic acid and alkyl (C_5-C_{10}) acrylate, commercially available under the tradename Carbopol ® 1623 from BF Goodrich

Polymer ** : Copolymer of acrylic acid and maleic anhydride, commercially available under the tradename Polygel® DB from 3V Chemical company

Fatty acid : C_8 - C_{18} fatty acid

nonionic : Capped ethoxylated carboxylate commercially available under the tradename Plurafac LF 231 from BASF

The invention is illustrated in the following non limiting examples, in which the following compositions are made by mixing the following ingredients in the listed proportions (weight %).

Example 1

The following compositions, according to the invention, were prepared:

Components	A	B	C	D	E	F
24 AS	1.0	2.0	2.0	2.0	1.0	1.0
C8 AS	1.0	2.0	1.0	2.0	2.0	2.0
Polymer *	0.8	0.8	1.2	1.0	1.0	1.5
Sulfamic acid	2.0	2.3	4.0	1.5	1.4	2.0
Caustic	-	2.5	2.5	2.0	1.4	-
Sodium hypochlorite	1.4	1.4	1.0	1.0	1.4	1.4
Fatty acid	-	0.1	0.3	0.3	0.2	-
Water and minors up to 100						

Example 2

The following compositions are in accordance with the invention

	G	H	I	J
C8 AS	1.0	1.0	2.0	2.0
24AE3S	2.0	2.0	1.0	1.0
Polymer *	0.8	1.0	1.2	1.0
nonionic	0.5	0.5	1.0	1.0
fatty acid	0.3	0.3	0.3	0.3
Sulfamic acid	2.5	3.0	3.0	2.5
Caustic	2.5	3.0	3.0	2.5
sodium hypochlorite	1.4	1.6	1.6	1.4
Water and minors up to 100				

Example 3

The following compositions are in accordance with the invention

	K	L	M
amine oxide	0.4	0.4	0.8
24 AS	-	2.0	2.0
C8 AS	2.0	2.0	2.0
Polymer *	0.8	0.8	0.8
Sulfamic acid	2.0	2.5	1.4
Caustic	1.5	2.5	1.4
Sodium hypochlorite	1.4	1.4	1.0
Water and minors up to 100			

Example 4

The following compositions, according to the invention, were prepared:

Components	N	O
24 AS	2.0	2.0
C8 AS	2.0	2.0
Polymer **	1.0	1.0
Sulfamic acid	2.3	1.5
Caustic	2.5	2.0
Sodium hypochlorite	1.4	1.0
Fatty acid	0.1	0.3
Water and minors up to 100		

What is claimed is:

1- A cleaning composition comprising a halogen bleach and an organic or inorganic $-NH_2$ compound, characterised in that said composition further comprises a polycarboxylate polymer.

2- The use of a polycarboxylate polymer in a cleaning composition comprising a halogen bleach and an organic or inorganic $-NH_2$ compound for providing reduced skin irritation.

3- A cleaning composition or use according to either one of Claim 1 or 2, wherein the molar ratio of said halogen bleach to said $-NH_2$ compound is from 10:1 to 1:10, preferably from 5:1 to 1:2, and more preferably from 3:1 to 1:2.

4- A cleaning composition or use according to any one of Claim 1-3, wherein said $-NH_2$ compound is a member selected from the group consisting of sulphamic acid, sodium sulphamate, potassium sulphamate, sulfamide, p-toluenesuphonamide, imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamide, and mixtures thereof and preferably is sulphamic acid.

5- A cleaning composition or use according to any one of Claims 1-4, wherein said polycarboxylate polymer is present in an amount of from 0.01% to 5% by weight of the composition

6- A cleaning composition or use according to any one of Claims 1-5, wherein said polycarboxylate polymer is a polyacrylate polymer.

7- A cleaning composition or use according to any one of Claims 1-6, wherein said polycarboxylate polymer has a total molecular weight of from 500,000 to 4,500,000, preferably from 1,000,000 to 4,000,000.

8- A cleaning composition or use according to any one of Claims 1-7, wherein said halogen bleach has the formula M(OX)y where :

a) M is a member selected from the group consisting of sodium, lithium, potassium, magnesium, calcium, and mixtures thereof;

b) O is an oxygen atom; and

c) X is a member selected from the group consisting of chlorine, bromine, iodine, and mixtures thereof; and

wherein y is 1 or 2.

9- A cleaning composition or use according to any one of Claims 1-8, wherein said composition further comprises from 0.1% to 95% by weight of a detersive surfactant.

10- A cleaning composition or use according to any one of Claims 1-9, wherein said composition is in liquid form.

11- A cleaning composition or use according to Claim 10, wherein said composition has a pH greater than 10, preferably greater than 11 and more preferably greater than 12.

12- A cleaning composition or use according to either one of Claim 10 or 11, wherein said composition is packaged in a spray dispenser, preferably in a trigger spray dispenser.

13- A method of cleaning a hard surface, wherein an effective amount of a composition as defined in any one of Claims 1 or 3-12 is applied onto said surface.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/17943

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 3/395, 3/37, 7/08

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/191, 238, 242, 245, 253, 263, 264, 269, 276, 280, 286, 318, 321, 337, 361, 362, 367, 369, 379, 380, 398, 402, 405, 434, 477

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS search terms: sulphamic, hypochlorite, polyacrylate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,997,587 A (BAUR ET AL) 05 March 1991 (05-03-91), column 2, lines 51-69, column 4, lines 25-32, column 6, lines 1-10.	1-3
Y,P	US 5,595,731 A (VALLIERES) 21 January 1997 (21-01-97), column 7, claims 5-9.	1-3
Y	US 4,992,195 A (DOLAN ET AL) 12 February 1991 (12-02-91), column 2, lines 25-60, column 3, line 45-column 4, line 65.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
12 DECEMBER 1997	29 JAN 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CHARLES BOYER Telephone No. (703) 308-0661

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

510/191, 238, 242, 245, 253, 263, 264, 269, 276, 280, 286, 318, 321, 337, 361, 362, 367, 369, 379, 380, 398, 402, 405, 434, 477